



Short communication

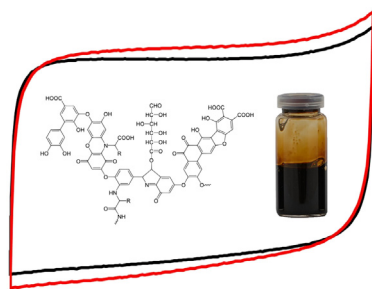
Humic acids as pseudocapacitive electrolyte additive for electrochemical double layer capacitors

Krzysztof Wasiński^a, Mariusz Walkowiak^{a,*}, Grzegorz Lota^{a,b,1}^a Institute of Non Ferrous Metals Division in Poznań Central Laboratory of Batteries and Cells, Forteczna 12, 61-362 Poznań, Poland^b Poznań University of Technology, Institute of Chemistry and Technical Electrochemistry, Piotrowo 3, 60-965 Poznań, Poland

HIGHLIGHTS

- Humic acids (HA) were applied for the first time as electrolyte additive for EDLC.
- Capacitances consistently rise with HA addition to 6 M KOH with maximum at 5 wt.%.
- Positive effect of humic acids has been ascribed to pseudocapacitive phenomena.
- Humic acids are described as low-cost, non-toxic and “green” electrolyte component.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel electrolyte additive for electrochemical capacitors has been reported. It has been demonstrated for the first time that addition of humic acids (HA) to KOH-based electrolyte significantly increases capacitance of symmetrical capacitors with electrodes made of activated carbon. Specific capacitances determined by means of galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy consistently showed increases for HA concentrations ranging from 2% w/w up to saturated solution with maximum positive effect observed for 5% w/w of the additive. The capacitance increase has been attributed to complex faradaic processes involving oxygen-containing groups of HA molecules. Due to abundant resources, low cost and easy processability the reported solution can find application in electrochemical capacitor technologies.

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1. Introduction

Electrochemical double layer capacitors (EDLC, also known as electrochemical capacitors) with electrodes made of high surface area carbon materials have been intensively investigated over the last decade as a promising power sources for the applications

where high power density is needed. In their purest form these electrochemical energy storage devices rely on energy stored in the form of electrostatic charge in the so-called electrochemical double layers formed on the electrode/electrolyte interfaces [1,2]. Activated carbons are considered as ideal electrode materials for EDLCs due to well developed surface area with favorable porous structure. When, in addition to purely electrostatic phenomena, faradaic processes contribute to the overall capacitance, the term supercapacitor is widely in usage and the excess capacitance is referred to as pseudocapacitance. Pseudocapacitance is most often brought about by redox-active surface species such as oxygen-containing functional groups of an activated carbon. Another potential

* Corresponding author.

E-mail addresses: mariusz.walkowiak@clao.poznan.pl, walkowiak@clao.poznan.pl (M. Walkowiak), grzegorz.lota@put.poznan.pl (G. Lota).¹ ISE members.

source of pseudocapacitance are redox active species dissolved in the electrolyte. As far as research on EDLCs is concerned, vast majority of effort has been focused to the development, modifications and characterization of carbonaceous electrode materials with relatively small attention devoted to the electrolyte composition [3,4]. Recent developments in this area include the addition of I^-/I_3^- redox pair [5,6], $K_3Fe(CN)_6/K_4Fe(CN)_6$ [7] and VO^{2+}/VO_2^+ redox pair [8] to aqueous electrolyte systems. Organic redox pair of hydroquinone/quinone in 1 M H_2SO_4 was described by Roldan et al. [9,10]. Lignosulfonates in sulfuric acid solution have recently been characterized by Lota et al. [11]. Indigo carmine in 1 M H_2SO_4 has also been reported [12]. Gel polymer electrolyte with sulfuric acid and poly(vinyl alcohol) was improved by *p*-benzenediol as an electrochemically active compound [13]. Redox-active electrolyte containing *p*-phenylenediamine in potassium hydroxide solution has been reported [14,15].

In the present work application of humic acids as the pseudocapacitive electrolyte additive is for the first time reported. Humic acids are an organic substance playing important role in the ecosystem, abundant in nature and easily recoverable from soil by means of simple extraction with alkali media. Precise chemical nature of HA is still under debate although they are typically viewed as a complex mixture of organic species, largely polymers with high molecular weights ranging from 1000 to 200 000 $g\ mol^{-1}$. Many authors [16–18] described HA as phenol rings bridged by alkyl chains with carbohydrate, amino acid, fat and protein residues including various ionic groups such as carboxylic acids and non-ionic polar alcohol, aldehyde, ketone, amide and amine groups. In spite of largely undeterminable precise molecular composition, HAs as a substance are relatively well recognized in scientific world due to their unquestionable biological role and can be obtained from natural sources by well defined routes. Redox properties of humic acids were investigated by Aeschbacher et al. [19]. Electrochemical measurements in three-electrode cells have proved that quinones are major redox-active functional group. The equilibrium of quinone/hydroquinone redox states was confirmed. As far as electrochemistry-related applications are concerned, carbon paste electrodes modified with HAs have been used for the determination of metal cations in aqueous solutions [20]. Complexation phenomena involving $LiOH$, $Co(NO_3)_2$ and humic acids were employed for the preparation of $LiCoO_2$ as Li-ion battery cathode material [21]. Also, $Li_3V_2(PO_4)_3/C$ composites were synthesized by using humic acid as reduction agent [22].

2. Experimental

Humic acids sample (commercial product utilized in agriculture, Rosier S.A., Belgium) has been dissolved in demineralized water. The mineral components have subsequently been removed by filtration. The product obtained after water evaporation and drying is an organic substance comprising practically exclusively a mixture of humic acids (HA) and their potassium salts. Fourier-transform infrared analysis of raw and purified HA were performed with Bruker FTIR spectrometer (model Equinox 55) on KBr pellets in the range from 400 to $4000\ cm^{-1}$ at $0.64\ cm^{-1}$ resolution. 1 mg HA sample was milled with 200 mg of KBr (spectrometry grade) followed by drying and pressing to obtain a transparent pellet. Each spectrum was corrected against pure KBr sample. Electrolytes have been prepared by dissolving the as-obtained HA (2 wt.%, 5 wt.% and 10 wt.%) in freshly prepared 6 M KOH. Pure 6 M KOH has been used as base line electrolyte. Specific conductivities have been determined at $25\ ^\circ C$ in thermostated two-electrode Swagelok-type cells with stainless steel electrodes and Teflon spacer (cell constant – $0.588\ cm^{-1}$) by means of electrochemical impedance spectroscopy technique. Nyquist plots obtained in the frequency range 100 kHz–

Table 1

Capacitances and conductivities measured by several techniques for 6 M KOH electrolytes with increasing humic acids concentrations.

Concentration of HA/%	Capacitance/ $F\ g^{-1}$					Conductivity/ $S\ cm^{-1}$
	CV		Galvanostatic		EIS	
	2 $mV\ s^{-1}$	200 $mV\ s^{-1}$	0.1 Ag^{-1}	2 Ag^{-1}	1 mHz	
0	89	30	108	68	108	0.627
2	92	42	112	83	110	0.579
5	98	45	117	89	114	0.458
10	97	42	114	85	113	0.347

1 Hz were fitted using EC-Lab software supplied with BioLogic VMP/3 instrument.

Electrodes containing 75 wt.% of commercial carbon Norit DLC Supra 50, 20 wt.% of binder (PVdF/HFP, Kynar Flex[®], Atofina) and 5 wt.% of acetylene black were prepared as pellets with geometric surface area of $0.8\ cm^2$. All the electrodes were dried in air at $60\ ^\circ C$ for 36 h followed by drying in vacuum oven at $100\ ^\circ C$ for another 12 h before the cell assembly. Typically, active mass of each electrode was 6.1–6.9 mg. The capacitors have been assembled in Swagelok type cells by sandwiching two electrodes with the separator made of a laboratory tissue paper. Capacitances have been determined at $25\ ^\circ C$ using multichannel potentiostat/galvanostat (Biologic VMP/3 with EC-Lab software) by means of three techniques. The cyclic voltammetry experiments were performed at the scan rates from 1 to $200\ mV\ s^{-1}$. The galvanostatic charge/discharge tests were conducted at current densities from 0.1 to $10\ A\ g^{-1}$. Cycling stability test was performed at $2\ A\ g^{-1}$. Electrochemical impedance spectroscopy (EIS) measurements were carried out using sinusoidal signal with 5 mV amplitude at frequencies ranging from 100 kHz to 1 mHz.

3. Results and discussion

Humic acids and their potassium salts dissolve in water based media to form dark brown solutions. It is difficult to determine precisely the solubility limit. Up to about 8 wt.% the solubility is excellent but when approaching 10 wt.% HA content the solution shows symptoms of near-saturation with traces of viscid agglomerates remaining even after long stirring. Importantly, conductivities of the solutions decrease visibly as the HA content increases, for the highest HA concentration being about half of the value measured for pure 6 M KOH (see Table 1). Specific conductivity measured for 6 M KOH equaled $0.627\ S\ cm^{-1}$, in accordance with standard literature data. Addition of HA results in a slight viscosity increase, which gives rise to the deterioration of ionic mobility.

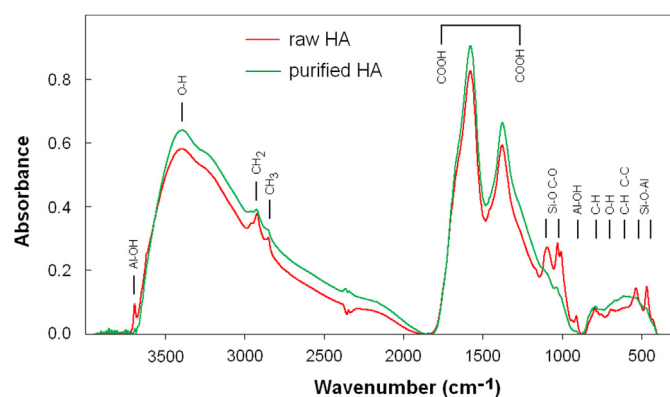


Fig. 1. FTIR spectra of raw and purified humic acids.

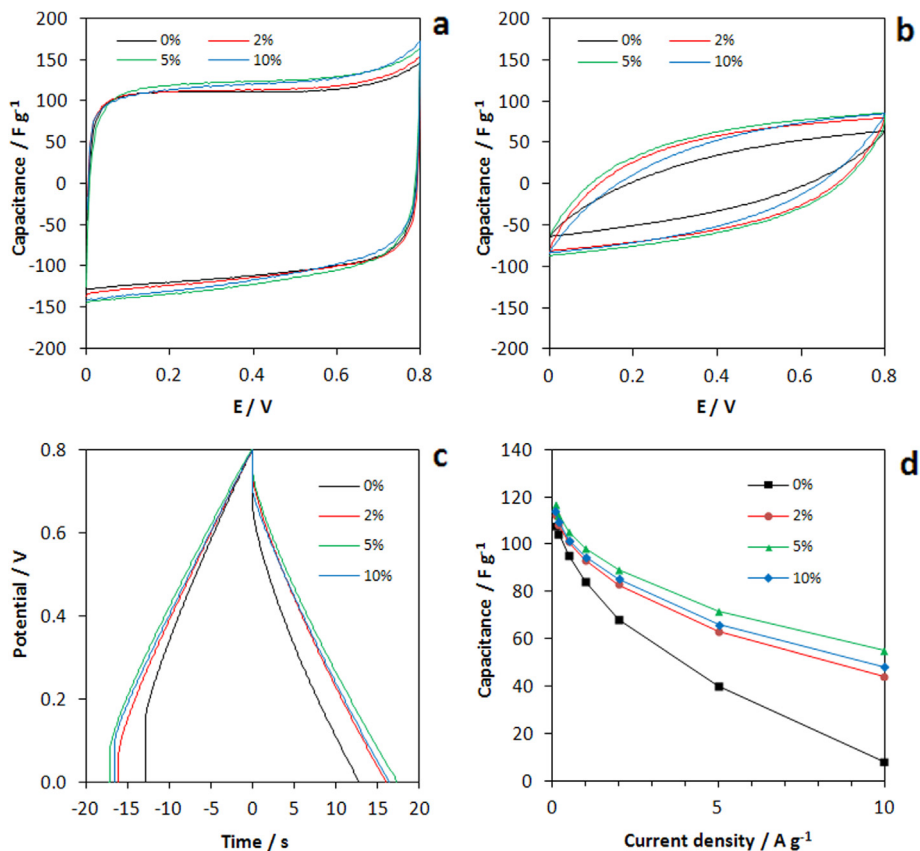


Fig. 2. Characteristics of EDLCs with 6 M KOH electrolytes with increasing HA concentrations: a) cyclic voltammetry at 2 mV s⁻¹, b) cyclic voltammetry at 200 mV s⁻¹, c) constant current charge/discharge at 2 A g⁻¹ (initial cycle), d) capacitances in function of current density.

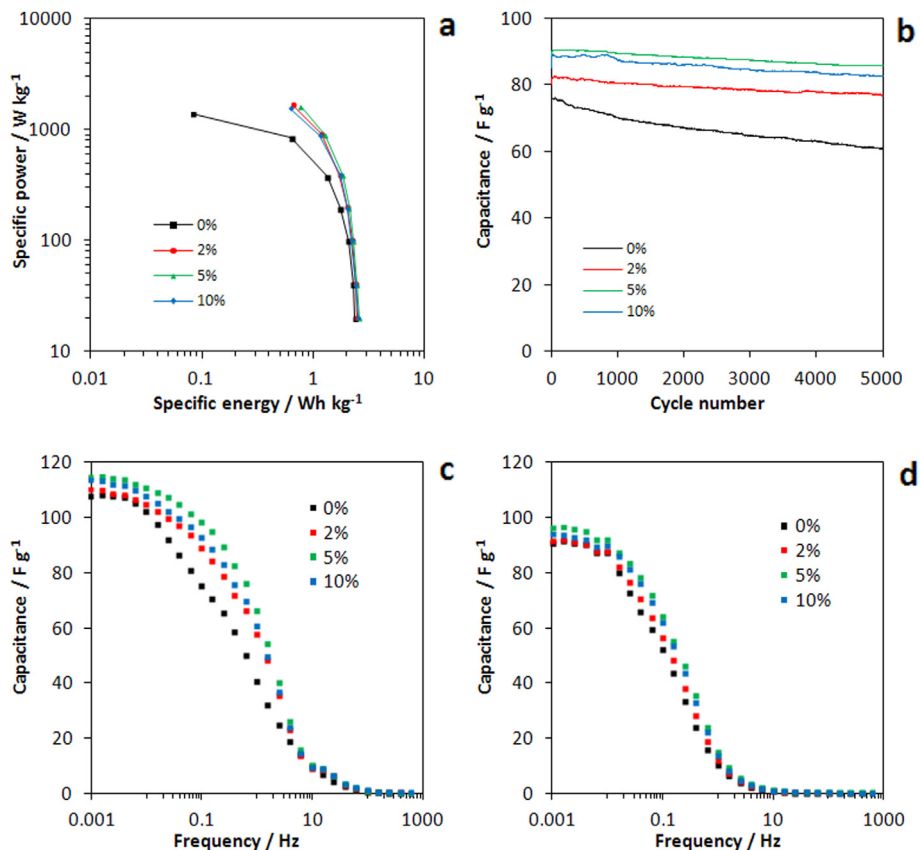


Fig. 3. Characteristics of EDLCs with 6 M KOH electrolytes with increasing HA concentrations: a) Ragone plot, b) constant current cycling stability test at 2 A g⁻¹, c,d) capacitances in function of frequency in EIS technique before and after 5000 constant current cycles at 2 A g⁻¹, respectively.

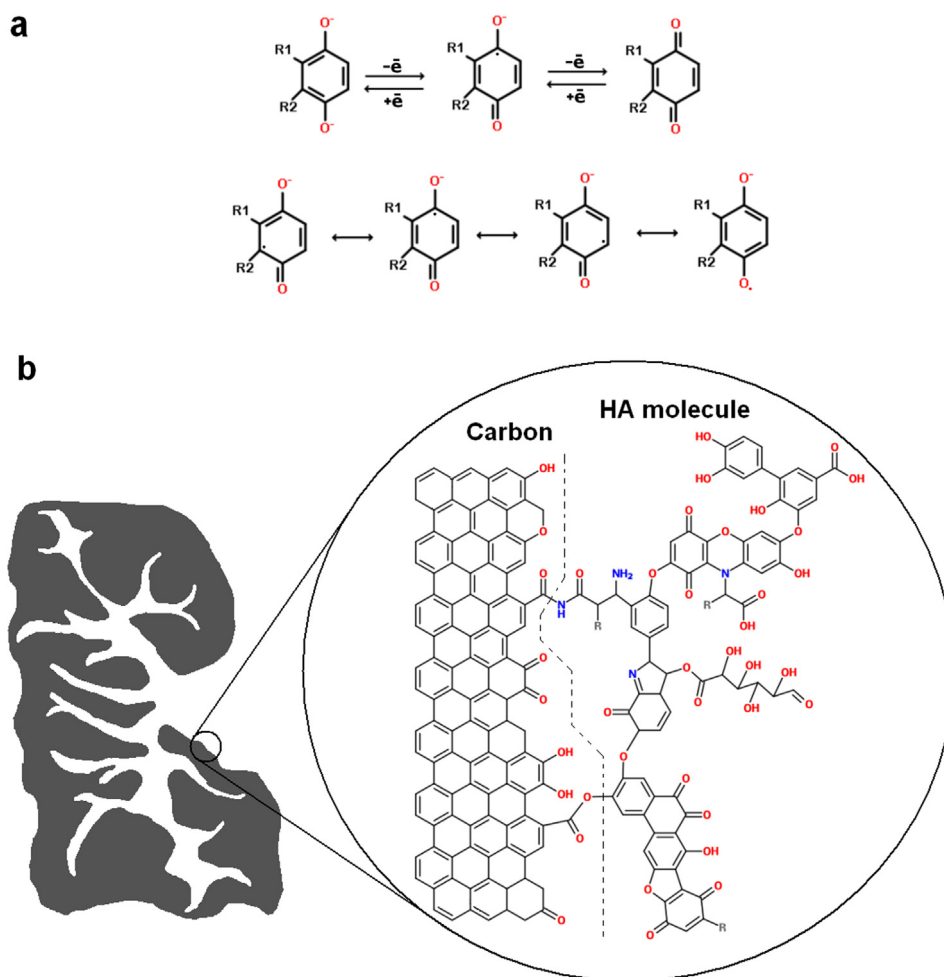


Fig. 4. Schemes of redox reactions involving quinone/hydroquinone pair and resonance equilibria of the quinone radicals (a) and schematic representation depicting the carbon electrode surface in HA containing electrolyte (b).

With increasing HA content specific conductivity of the solution decreases steadily to reach 0.347 S cm^{-1} in the case of 10% HA.

Fig. 1 shows FTIR spectra recorded for the raw and purified HA samples. Considering the purified HA, the substance exhibits several signals attributable to oxygen containing groups such as H bonded OH at $\nu = 3400 \text{ cm}^{-1}$, COOH asymmetric stretching at $\nu = 1580 \text{ cm}^{-1}$, symmetric stretching at $\nu = 1380 \text{ cm}^{-1}$, C–O stretching and O–H deformation of COOH groups at $\nu = 1200 \text{ cm}^{-1}$, stretching of carbohydrate or alcoholic bonds at $\nu = 1050 \text{ cm}^{-1}$. Apart from that, aliphatic C–H stretching of alkyl groups at $\nu = 2914 \text{ cm}^{-1}$, stretching of methyl C–H groups at $\nu = 2852 \text{ cm}^{-1}$, plane vibrations of aromatic C–H, benzene and alkyl benzene bonds at $\nu = 900\text{--}700 \text{ cm}^{-1}$. Importantly, spectrum of purified HA does not contain signals from Al–OH (aluminosilicates), Si–O (silica, quartz) and Si–O–Al (aluminosilicates) characteristic for raw (unpurified) HA sample.

Fig. 2a and b shows CV curves of the tested capacitors at two scan rates – 2 and 200 mV s^{-1} . Respective capacitance figures are collected in Table 1. As can be seen, capacitances clearly tend to increase with HA addition up to 5% and then slightly drop for both scan rates. This behavior can consistently be observed also for other scan rates (not shown in this work). Galvanostatic charge/discharge tests confirm this observation. Fig. 2c presents galvanostatic characteristics for initial cycles and respective capacitances are shown in Table 1 for two current densities. Here also 5% HA is the point of maximum capacitance. For the assessment of rate performance

capacitances have been determined in function of current density (see Fig. 2d). It is evident that cells with HA-based electrolytes show significantly enhanced rate capability in comparison to the cell with base line KOH electrolyte. For an extremely high current density of 10 A g^{-1} HA addition still allows for retention of ca. 50% of the low-current capacitance. Fig. 3c shows cyclic galvanostatic tests at a high current density of 2 A g^{-1} . Cells with HA based electrolytes not only exhibit markedly higher capacitances over the entirely cycle life but also their capacitances drop more slowly over 5000 cycles as compared to the cell with reference electrolyte. Electrochemical impedance spectroscopy technique has been applied for the determination of capacitances before and after galvanostatic cycling (5000 cycles at 2 A g^{-1}). Table 1 presents numerical data for 1 mHz (before cycling). The positive effect of HA addition is generally confirmed by this study. After harsh long-term cycling the cells' behavior somewhat worsens but the HA effect is still clearly visible.

As has been demonstrated above, measurements carried out by three different techniques and in variable conditions consistently prove that addition of humic acids to KOH-based electrolyte leads to enhancement of electrochemical characteristics in terms of capacitances, rate capability and cycle life. Ragone plot shown in Fig. 3a helps to position the HA containing cells versus base line cell in terms of specific energy and specific power.

The maximum positive impact has been found for 5% HA concentration. Above this threshold decreasing conductivity starts to

deteriorate the ionic mobility and hence slight decrease of capacitances. We attribute the described effect to pseudocapacitive phenomena brought about primarily by the presence of redox-active species on HA molecules, such as quinone/hydroquinone groups (compare [19] and [23]). Although characteristic signals from quinone groups are not revealed among other oxygen group signals on the FTIR spectrum, their presence can be regarded as certain based on the evidence provided for example by Scott et al. [24] from electron spin resonance measurements. Additionally, in the strongly basic medium free radicals may play important role in the quinone redox activities, according to the scheme proposed in Fig. 4a. The quinone radical is known to be stabilized by resonance depicted in Fig. 4b [25]. In our opinion the involvement of free radicals may account for an extraordinarily high reaction rates which manifest themselves in the observed enhancement of rate capability (compare Fig. 2d). This behavior is hard to explain only on the basis of typical redox reaction which should rather slow down the overall process, as opposed to purely electrostatic phenomena. Fig. 4c provides a probable view of what happens on the carbon electrode/electrolyte interface in our HA containing system. Owing to a large concentration of chemically reactive oxygen groups, including carboxyl, phenolic and alcoholic hydroxyls (as evidenced above) the HA species will tend to interact chemically and/or physically with the chemically similar carbon surfaces, providing conditions for redox-type interactions [23]. Involvement of hydrogen bond based interactions is likely to contribute to complex process kinetics. It is also possible that HA species will form stable covalent bonds with the surface species of carbon. Such a monolayer of HA species might result in the increase of oxygen functional groups exposed to the electrolyte, increase of hydrophilicity of carbon interface and, last but not least, substantial modification of the electrical double layer structure in a way that is still to be understood. Due to complex chemical nature of humic acids the full picture of the processes involve in fact a multitude of phenomena and mechanisms. Systematic study of these phenomena and mechanisms is going to be the subject of future in-depth studies.

4. Conclusions

Humic acids have been examined as additive for KOH based electrolyte for electrochemical double layer capacitors with activated carbon electrodes. With increasing HA content specific conductivities decrease steadily due to increasing viscosity. Despite of this, capacitances of the electrochemical capacitors increase significantly with the HA addition with maxima observed always at 5 wt.% HA in the electrolyte. This effect has been confirmed by cyclic

voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy and is independent of experimental conditions, being even more pronounced for very high galvanostatic cycling rates. Addition of HA also gives rise to an enhancement of cycling stability which has been evidenced over 5000 cycles at 2 A g^{-1} . Positive influence of HA is clearly attributable to pseudocapacitive phenomena brought about by redox-active functional groups on HA molecules. Humic acids can be considered as low cost, environmentally friendly and non-toxic electrolyte component of electrochemical double layer capacitors, asymmetric and hybrid capacitors.

Acknowledgments

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